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CONTAMINATION OF PESTICIDES RESIDUES ON GRAPE GROWING SOILS IN NASHIK DISTRICT

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ABSTRACT

Nashik district being one of the highest producers of grapes in Maharashtra constitutes the most probable area with the highest use of chemical pesticides to enhance grape production. Pesticide residues were determined in soils collected from grape growing areas of Nashik District. Soil samples were collected from different villages of leading grape growing areas of Nashik district. An analytical multiresidue method for the simultaneous determination of various classes of pesticides in soil was done by using LCMS/MS and GCMS/MS instruments on Multi Reaction Monitor (MRM) mode. Pesticides were extracted from soil with ethyl acetate. Pesticides were detected in all the soil samples collected. Spiked blank samples were used as standards. Pesticides were confirmed by their retention times. Recovery studies were performed at 10 and 20 ppb fortification levels of each pesticide, all the recoveries are above 70% with a relative standard deviation between 0.31 and 6.4%.

Concentration and percent contamination of pesticide residues in soilwere determined .In the tested soil samples, residues of various pesticides were found, the pesticides which are found in notable amount are: Carbendazim (3.68-86.8 ppb, 100%), Azoxystorbin (1.96-35.2 ppb, 20 %), Imidacloprid (1.47-31.5ppb,86.66%), Flusilazole 0-.07ppb,6.66%), Dimethomorph (1.84-63.7, 86.66%), Thiamethoxam (1.09-24.8, 33.33%) , Fenamidone (4.26-13.8,20%), Pyraclostorbin (1.2-23.7,33.33%), Clothianidin (1.47-7.92 , 33.33%) Iprovalicarb (1.13-65.6, 26.66%), Hexaconazole (2.6-4.89, 20%), Kresoxim methyl (0-7.69, 6.66), Tridemefon (0-28.8, 6.66%), Penconazole (0-2.48, 6.66%), Spinosad A (0-2.15, 6.66%), etc. Apart from this during our study to our great surprise in two soil samples we have found the residues of pp-DDE1, pp-DDT1, pp-DDD an isomer of DDT (1.9-5.5ppb) which are already banned. The presence of banned pesticide residues in soil samples is a matter of concern for future food chain accumulation and human health also.

The present study generates the data on the pesticides residues levels in grape growing soils of Nashik district, which will be highly useful to create awareness among the farmers about non-judicious and excess application of pesticides.

KEYWORDS: Pesticides, Multiresidue Pesticide Analysis, LCMS/MS and GCMS/MS

INTRODUCTION

Intensive agricultural practices often include the use of pesticides to enhance crop yields. However the improvement in yield is sometimes concomitant with the occurrence and persistence of pesticide residues in soil and water [1]. Pesticides may reach the soil through direct application to the soil surface, incorporation in the top few inches of soil, or during application to crops [2]. Pesticides can enter ground water resources and surface run-off during rainfall, there by contributing to the risk of environmental contamination. The fate of pesticides in soil is influenced by the physico-chemical properties of the pesticide, the properties of the soil (presence of clay materials, organic matter, and pH), climate, biology, and other factors [3].The increased use of pesticides has caused pollution of soils and water worldwide.

About 60 percent population in India is involved in agricultural sector which contributed to a very important part of Indian economy. Several pesticides including organochlorine, organophosphate, carbamate, fungicides, herbicides and synthetic pyrethroids are used in modern agricultural production to meet the need for abundant, safe and affordable food and fiber. Although the use of pesticides has led to increased agricultural production but, their use has also been associated with several concern, including risk to human health and environment [4]. These compounds have a wide range of both acute and chronic health effects, including cancer, neurological damage, reproductive effects, immune suppression, birth defects, and are also suspected endocrine disruptors [5, 6].During the last few decades, widespread contamination and toxic effects of organic chemicals have becomes a serious environmental problem. They enter the soil by direct treatment or being washed off from the plant surface during rainfall. Their physico-chemical characteristics, which include hydrophobicity and resistance to degradation, make these chemicals to accumulate in soils and sediments. Soil and sediments can act as a contributor of organic pollutants to the atmosphere, especially of semi volatile compound in warm climates. The fate of pesticides in soils with different cropping land use has been extensively studied worldwide including India [7-11].Excessive use of chemicals has put forth question mark on sustainability of agriculture by contaminating the soil and declining food quality[12] .Pesticide consumption in Grape farms is on higher side. A plant retains only half of this applied spray as the leaf creates a non-wetting interface for the pesticide. The remaining pesticide runs off and contaminates soil and water and affects terrestrial and aquatic life. [13].

Out of total geographical area of Nashik district 8, 65,000 ha are under grape cultivation. About 60-70% of total production of seedless grapes are produced in Nasik district .Out of 15 talukas from Nasik district, 90% of grape production are from Nasik, Niphad and Dindori .These are leading growers of grapes. Percentage of pesticides consumption for grapes in these areas are on higher side .Out of 10-12 metric tonnes of grapes produced every year , the export rate tunes to only 1% due to excess application of pesticides which, declines quality of grapes. [14].

This work is focused on the determination of the pollution levels by pesticides in soils of grape farms in Nashik district. For this reason we propose a multiresidue method to monitor pesticide residues, due to wide diversity of pesticides used in this region. Also this paper describes a sensitive method for the extraction and analysis of the target pesticides in soils by LC-MS in a single run. The LC-Ms method described in this work is rapid and allows the simultaneous determination of higher number of compounds than previously published methods in a single run

A survey about pesticide - use-practices was conducted at the same time of sample collection with the help of structural questionnaire. Survey results indicated that farmers are using highly toxic pesticides. Farmers reported that they did not always use pesticides in an appropriate manner. These improper practices may result in the contamination of the environment by pesticides.

EXPERIMENTAL

Study Area

3 major grape growing talukas from Nasik district as, Niphad, Dindori, and Nasik was selected because these are leading growers of grapes. Percentage of pesticides consumption for grapes in these areas is on higher side.

Soil Sampling

Sampling equipments (soil auger, spade bucket, plastic sheet, and plastic bags) are used. 5 soil samples from different villages of each taluka were collected by proper soil sampling method [15] in such a way that, 2 samples from export quality grape growing field and 3 samples from random field. Soil samples were collected from the study areas in November-December 2012. The composite soil samples were drawn from 0-15 cms depth. Samples were collected from

the vinerow where most of the vine roots are located using stainless steel auger. The subsamples were placed into a 16-liter bucket, 4-5 samples from each location were thoroughly mixed on a plastic sheet to ensure that the soil collected was truly representative of each location, then air-dried, grounded and sieved through a mesh with a grain size of 2 mm. Samples were packed in air tight plastic bags, codes are given as, A to O for 15 samples and then samples are transported ice preserved to the laboratory until further chemical processing.

Sample Extraction Procedure

Samples are extracted by validated method [16-17]

Sample Extraction for LCMS/MS Analysis

10g soil sample, 5 ml water, 10 ml ethyl acetate and 10 g sodium sulphate anhydrous were homogenizing it for 2 min at high speed and centrifuge for 5 minutes at 50000 rpm. 3 ml of the ethyl acetate phase was taken into a centrifuge tube containing 25mg primary secondary amine Shake vortex for 1 min. Centrifuge at around 5000 rpm for five minutes. 2 ml cleaned supernatant was takem and0.2 ml 10% diethylene glycol was added with methanol to it .Evaporate it under gentle stream of nitrogen using low volume concentrator at 35^0C.Reconstitute into 1 ml methanol and 1 ml 0.1% acetic acid in water. Centrifuge at 10000 rpm for 5 min and filter through 0.2 µm PVDF/nylon membrane filter. Inject 10 µl into LCMS/MS.

Sample Extraction for GCMS/MS

1 ml extract was taken and clean it with 25 mg PSA. Centrifuge at 10000 rpm and filter through 0.2 µm PTFE membrane filter. Inject 2 µl (split less injection mode) into GCMS/MS.

Instrumental Analysis

Samples were analyzed by multiresidue pesticide analysis with the help of GCMS/MS and LCMS/MS.

Chemicals

Methanol & Water (HPLC Grade) of J T Backer (as a Mobile phase). Chilled Distilled water (to maintain the temp. of matrix as increase in temp cause degradation of some pesticides residues and Ethyl Acetate (to prevent degradation of some PRs in Extraction), PSA (Primary secondary amine for cleaning of matrix interference in sample), Activated Sodium sulphate (to remove water traces), Formic Acid (to acidify extraction solvent), Ammonium formate (as a buffer for mobile phase), all these were purchased from Merk. 10% DEG (Di ethylene glycol) in methanol (as a analytes keeper & protector in MS). Acetic acid (to acidify final volume) and PTFE (Polytetrafluoroethylene) Filter of 0.22 µm (used to filter final injection volume before going to fill vial).

Pesticide Standard

The certified Pesticides standards were purchased from (Dr. Ehrenstorfer GmbH, Germany). The purity of all pesticide standards were greater than 95%. All standards were tuned to obtain optimized MRM and qualifier (for confirmation of PR) for analysis filter.

Preparation of Standards

5.0 mg of pesticide standards makeup with ethyl acetate for GCMS/MS compounds and methanol for LCMS/MS compounds in to 5 ml volumetric flask. The solution concentration is around 1000 mg / litre prepares the working standard (mix standard) of concentration 1.0 mg/litre and does the subsequent dilution with respective solvent. Theses individual

standard stock solutions were mixed appropriately to obtain desire concentration of Pesticides and then stock solution of standard mix was serially diluted with methanol to 1 µg/ ml. Separation and Quantification of organochlorines was carried out using GCMS (Perkin Elmer, Clarus500) with auto sampler equipped with an Electron Capture Detector (ECD' 63Ni),while Quantification of other pesticides was carried out using LCMS/MS(Absciex, 4000 Q TRAP) **.**

Analysis on GCMS/MS

GCMS/MS conditions are as follows

GC Conditions

Column: DB 5, MS 0.25 µm, 30m x 0.25 mm id. Carrier gas: Helium. Constant flow: 1 ml / min. Injection: 2 µl / split. Injector temperature: 250^0C (manual / auto sampler mode).

Analysis on LCMS/MS

HPLC Conditions: Two mobile phases are used

A: 5 mM ammonium formate dissolved in water: methanol (80:20) (157.7 mg ammonium formate dissolved in 500 ml of mobile phase).

B: 5 mM ammonium formate dissolved in methanol: water (90:10) (157.7 mg ammonium formate dissolved in 500 ml of mobile phase) .Analytical column: Zorbex (Eclipced plus-C18)3.5µ, 4.6 x 100 mm (API 4000).Flow rate: 0.6 ml/min.

Mass Conditions: Interface: ESI + ve .Source température: 450^0C

Analytical Quality Control

The certified Pesticides standards were purchased from (Dr. Ehrenstorfer GmbH Germany) used for calibration of the instruments. The concentrations of analyte were determined by comparing the peak area of the samples and five level calibration curves of the standards. The correlation coefficient of calibration curves were ranged from 0.9980 to 0.9990.The pear identification was conducted by the accurate retention time of each standard. A results above Limit of Detection (LOD) were taken for calculations and below (LOD) were taken as zero (0) in the calculations. .

Validation of the Methodology

The method was validated in soil samples by analysis of spiked samples. The identification of the target pesticides was carried out by searching in the appropriate retention time windows (RTWs), The quantification of the samples was carried out by injecting blank sample extracts spiked with the pesticides at five different concentration levels to perform the calibration curves. Spiked blank samples were used as standards. Pesticides were confirmed by their retention times, Recovery studies were performed at 10 and 20 ppb fortification levels of each pesticide, and the recoveries are above 70% with a relative standard deviation between 0..31 and6.4%.

The calibration data obtained are shown in Tables 1.

Calculation: Concentrations i.e. contaminations of pesticide residues were determined by using peak areaof standard ,peak area of sample, concentration of standard as well as weight of sample.

RESULTS AND DISCUSSIONS

Several studies[18] reported the detection of pesticides and herbicides in soils from agriculture areas of Delhi region and most frequent pesticides detected were organochlorine group which is more persistent and decomposed very slowly. In Jalgaon district the presence of pesticide residues was reported by[19] by using technique GCMS.

Several multiresidue methods for a large number of pesticides, by gas chromatography (GC) coupled to mass spectrometry (MS) have been published suitable for soil samples. However, the cited liquid chromatography (LC) coupled to mass spectrometry (MS) multiresidue methods applied to environmental samples can detect fewer pesticides in a single run than GC-MS methods. Furthermore there are very few published multiresidue methods using LC with a single quadrupole.

Table 1: Linear Range, Recoveries, R. S. D., LOD and LOQ for Soil Samples Pesticides

Analyte	Linear Range (µg/kg)	R^2	Recovery (%) [a]	R.S.D (%)[a]	Recovery (%)[b]	R.S.D. (%)[b]	LOD (µg/kg)	LOQ (µg/kg)
Carbandazim	5-100	0.99	80.7	1.18	98.3	0.31	0.3	1.0
Azoxystrobin	5-100	0.99	82.66	3.93	78.66	2.19	0.3	1.0
Imidacloprid	5-100	0.99	82.73	1.56	82.76	0.69	0.6	2.0
Flusilazole	5-100	1.00	79.2	3.09	82.76	0.69	0.5	1.5
Dimethomorph	5-100	0.99	101.9	2.76	93.066	0.81	0.6	2.0
Thiamethoxam	5-100	0.99	55.26	1.41	61.36	2.69	1.0	2.5
Fenamidone	5-100	0.99	73	2.99	105.66	0.55	0.5	1.5
Pyraclostrobin	5-100	1.00	81.066	2.49	77.33	1.47	0.3	1.0
Clothianidin	5-100	0.99	82.6	3.85	85.4	1.05	0.6	2.0
Iprovalicarb	5-100	0.99	66.76	1.81	104.33	1.11	0.3	0.1
Hexaconazole	5-100	0.99	76.83	2.87	91.73	0.88	0.5	1.5
Kresoxim Methyl	5-100	0.99	86.76	3.08	74	3.39	0.3	1.0
Tridemefon	5-100	0.99	80.76	7.59	95.5	1.27	0.3	1.0
Penconazole	5-100	0.99	81.56	3.06	67.3	2.19	0.6	2.0
Spinosad A	5-100	0.99	75.03	4.76	73.83	2.69	0.3	1.0
Metalaxyl	5-100	0.99	95.1	4.51	92.73	1.74	0.3	1.0
Tetraconazole	5-100	0.99	89.4	2.8	95.7	1.04	0.5	1.5
Myclobutanil	5-100	0.99	84.2	4.94	99	0.93	0.3	1.0
Acetamiprid	5-100	0.99	88.2	0.63	99.23	0.76	0.6	2.0
Atrazine	5-100	0.99	75	0.58	77.76	2.77	0.3	1.0
Carbaryl	5-100	0.99	97.1	3.54	78.56	2.72	0.3	1.0
Carbofuran	5-100	0.99	71.13	0.71	93.56	1.7	0.3	1.0
Dimethoate	5-100	0.99	83.16	0.78	76.93	1.67	0.5	1.5
Etrimphos 1	5-100	0.99	85.63	6.14	85.86	6.14	0.3	1.0
Iprobenphos 1	5-100	0.99	88.03	1.69	75.03	3.9	0.6	2.0
Phosalone 1	5-100	0.99	74.43	1.96	82.33	2.52	0.5	1.5
Propiconazole	5-100	0.99	81.6	3.01	91.1	2.12	0.6	2.0
Simazine	5-100	0.99	78.9	9.4	84.6	1.84	0.5	1.5
Tebuconazole 1	5-100	0.97	88.9	3.13	80.4	3.25	0.6	2.0
Triazophos 1	5-100	0.99	94.4	2.81	97.56	4.08	0.3	1.0
Trifloxystrobin 1	5-100	0.99	72.6	2.29	84.66	1.38	0.3	1.0
3-Hydroxy Carbofuran 1	5-100	0.98	87.26	1.62	99.43	1.73	0.3	1.0

[a] 10 **µg/kg**[b] 20 **µg/kg**

The quantification of the samples was carried out by injecting blank sample extracts spiked with the pesticides at five different concentration levels to perform the calibration curves. The linearity of the calibration curves was studied

using both peak height and peak area and better quantification results were obtained when peak area was considered. Calibration data obtained are shown in Tables 1. Good linearity of the response was found for all pesticides at concentrations within the tested interval, with linear determination coefficients higher than 0.97 in soil samples. Limit of Detections (LODs) and Limit of Quantification (LOQs) were determined as the lowest pesticide concentration injected that yielded a signal-to-noise (S/N) ratio of 3 and 10 (when the quantification ion was monitored), respectively. LOD values ranging from 0.3 to 0.6 µg/kg , were obtained for water and soil samples, respectively. LOQ values lower than 5 µg/kg were obtained for water and soil samples, respectively (Tables 1).

A study of recovery for each pesticide in each matrix at a low concentration level was performed in order to assess the extraction efficiency of the proposed methods. For this purpose ten blank samples were spiked with the target analytes, at 10 µg/kg, 20µg/kg respectively. Recoveries higher than 70.0% were obtained for all pesticides in soil samples. Soil sampleswas also evaluated at two concentration levels, and expressed as relative standard deviation (R.S.D. %); values lower than or equal to 10% were obtained for all compounds.

Table 2: Concentration of Pesticides Residues in Soil Samples All Values are in ppb (µg/kg)

Sr. No.	Name of Pesticides	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1	**Carbandazim**	53.6	86.8	4.53	7.5	14.5	46.2	78.5	430	14.5	64	7.95	18.2	69.9	3.68	10.9
2	**Azoxystorbin**	0	0	0	0	0	0	0	0	35.2	0	0	2.92	1.96	0	0
3	**Imidacloprid**	4.3	5.32	5.76	0	26.5	19.5	19.1	2.83	17.2	0	23.5	1.47	31.5	12.6	6.77
4	**Flusilazole**	0	0	0	0	0	0	0	0	2.07	0	0	0	0	0	0
5	**Dimethomorph**	1.84	7.39	0	0	36.4	45.8	14.8	6.24	63.7	7.17	45.1	46.4	20.9	1.63	3.34
6	**Thiamethoxam**	0	0	24.8	0	0	0	1.71	0	15	0	5.46	0	1.65	1.09	0
7	**Fenamidone**	0	0	0	0	0	4.26	0	0	13.8	0	0	0	0	0	0
8	**Pyraclostorbin**	0	1.2	12.8	0	2.68	3.48	0	0	23.7	0	0	0	2.22	0	0
9	**Clothianidin**	0	0	0	1.98	0	0	5.37	0	1.47	0	2.71	0	0	7.92	1.85
10	**Iprovalicarb**	0	0	0	0	1.13	13.7	0	0	65.6	0	2.54	0	0	0	0
11	**Hexaconazole**	0	0	0	0	0	3.23	0	0	2.6	0	4.89	0	0	0	0
12	**Kresoxim methyl**	0	0	0	0	0	0	0	0	7.69	0	0	0	0	0	0
13	**Tridemefon**	0	0	0	0	0	0	0	0	28.8	0	0	0	0	0	0
14	**Penconazole**	0	0	0	2.48	0	0	0	0	0	0	0	0	0	0	0
15	**Spinosad A**	0	0	0	0	0	0	0	0	2.15	0	0	0	0	0	0
	Total	**59.74**	**100.71**	**47.89**	**11.96**	**81.21**	**136.17**	**119.48**	**439.07**	**291.33**	**71.17**	**92.15**	**68.99**	**128.13**	**26.92**	**22.86**

Note: zero (0) stands for “pesticides not detected” and it is include in calculating the mean, A to O are soil sample codes.

The quantity of pesticide residues detected in the soil samples collected from different location of Nashik district is reported in Table 2.Chromatogram of multiresidue pesticides reported in Figure 1. A total of 15 samples were collected from different location of Niphad, Nashik, Dindori and analyzed for the pesticide residues. Most of the soil samples were found contaminated with pesticide residues at different levels. The most widely detected pesticide was Carbandazim found in all the The soil sample I was found to be contaminated by all the pesticides.

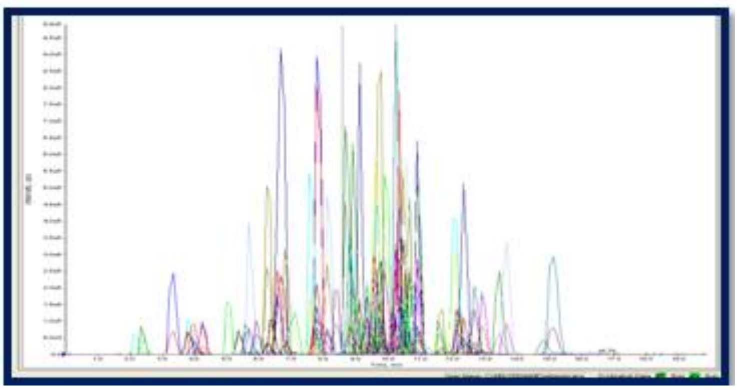

Figure 1: Chromatograms of All Pesticide Residues in Soil on LCMS by Multiresidue Pesticide Analysis

Table 3: Information about Pesticide Residues Detected in Soil Samples

Sr. No.	Name of Pesticides	Class of Pesticide	Group of Pesticide	Molecular Formula	Retention Time(RT) Minute	Range (ppb)	Found Samples Contaminated	Percentage Contamination (%)
1	Carbandazim	fungicide	Benzimidazole	$C_9H_9N_3O_2$	6.86	3.68-86.8	15	100
2	Azoxystorbin	fungicide	Strobilurin	$C_{22}H_{17}N_3O_5$	9.2	1.96-35.2	03	20
3	Imidacloprid	Insecticide	Nicotinoids	$C_9H_{10}ClN_5O_2$	5.15	1.47-31.5	13	86.66
4	Flusilazole	fungicide	Triazole	$C_{16}H_{15}F_2N_3Si$	10.38	0-2.07	01	6.66
5	Dimethomorph	fungicide	Morpholine	$C_{21}H_{22}ClNO_4$	9.77	1.84-63.7	13	86.66
6	Thiamethoxam	Insecticide	Nicotinoids	$C_8H_{10}ClN_5O_3S$	4.1	1.09-24.8	06	33.33
7	Fenamidone	fungicide	Imidazole	$C_{17}H_{17}N_3OS$	9.4	4.26-13.8	02	20
8	Pyraclostorbin	fungicide	Strobilurin	$C_{19}H_{18}ClN_3O_4$	10.88	1.2-23.7	06	33.33
9	Clothianidin	Insecticide	Nicotinoids	$C_6H_8ClN_5O_2S$	5.4	1.47-7.92	06	33.33
10	Iprovalicarb	fungicide	Carbamates	$C_{18}H_{28}N_2O_3$	10	1.13-65.6	4	26.66
11	Hexaconazole	fungicide	Triazole	$C_{14}H_{17}Cl_2N_3O$	10.9	2.6-4.89	03	20
12	Kresoxim methyl	fungicide	Strobilurin	$C_{18}H_{19}NO_4$	10.66	0-7.69	01	6.66
13	Tridemefon	fungicide	Triazole	$C_{14}H_{16}ClN_3O_2$	9.8	0-28.8	01	6.66
14	Penconazole	fungicide	Triazole	$C_{13}H_{15}Cl_2N_3$	10.6	0-2.48	01	6.66
15	Spinosad A	Insecticide	Natural Product Derivative	$C_{41}H_{65}NO_{10}$	13.86	0-2.15	01	6.66
16.	pp-DDE1	Insecticide	Organochlorine	$C_{14}H_8Cl_4$	21.38	5.2-5.5	02	20
17.	pp-DDT1	Insecticide	Organochlorine	$C_{14}H_9Cl_5$	22.92	2.0-2.5	02	20
18.	pp-DDD	Insecticide	Organochlorine	$C_{14}H_{10}Cl_4$	24.27	1.9-3.2	02	20

Table 4: Contamination of DDT Isomers (ppb or ng/ml) in Soil Samples from Selected Grape Farms in Nashik District

Sr. No	Soil Sample Code	Name of Pesticides	Concentration ppb (μg/kg)	Retention Time	Peak Area	Precursor Ion(m/z)	Product Ion (m/z)	Corelation Coefficentr^2
1	C	pp-DDE1	5.2	21.38	1136.774	208	63	0.9972
		pp-DDT1	2.0	22.92	451.884	266	133	0.9946
		pp-DDD	1.9	24.27	140.097	246	176	0.9977
2	N	pp-DDE1	5.5	21.38	1218.859	235	165	0.9978
		pp-DDT1	2.5	22.92	567.015	235	165	0.9963
		pp-DDD	3.2	24.27	210.357	235	165	0.9930

The data showed that the selected grape growing soil samples were found to be more contaminated by fungicides may be because of pests observed in vineyards are mostly of fungus category such as **Downy mildew** (Plasmopora viticola), **Powdery mildew** (Uninula necator), **Black rot** (Guignardia bidwellii), **Anthracnose** (Elsinoe ampelina) therefore, use of fungicides contributeson higher side in vineyards results in more contamination.

Table 4 shows the presence of DDTa long banned organochlorine insecticide and it's isomers (DDE,DDD) in soil samples C and N are detected on GCMS/MSin notable amount.Figure 2 shows chromatograms of DDT and its isomers. Increase in the concentration of organochlorine molecules up the food chain, with bioaccumulation and biomagnifications taking place in higher organisms including man had been reported. Despite the ban pronounced on most of these toxic organochlorine compounds, they are still being used in most developing nations both domestically and on agricultural crops. This continued use of organochlorine pesticides has remained a matter of international concern because of their persistence and long-distance carriage through oceanic currents and atmospheric transports identified the high potency/efficacy and lower cost of organochlorine pesticides compared with alternative pesticides as the reasons for their

continued use in most developing countries. The main use of the pesticides in these countries is their application as insecticides on cash crops.

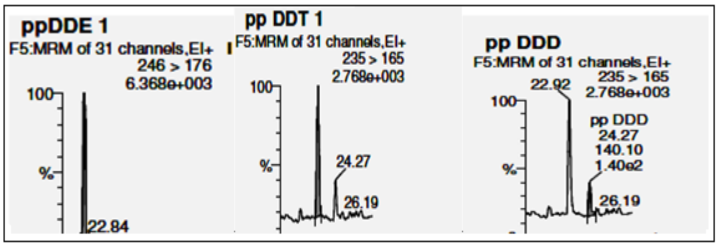

Figure 2:Chromatograms of DDT Isomers Detected in Soil Samples

CONCLUSIONS

In the present study the detection of pesticide residues in grape growing soil from different villages of nashik district demonstrated the diffrence in pesticide residues could me related to the fate of pesticides in soil is influenced by the physico-chemical properties of the pesticide, the properties of the soil (presence of clay materials, organic matter, and pH), climate, biology, as well as different time of application of pesticides .

The residues of pp-DDE, an isomer of DDT were detected in soil samples which were already banned. The presence of banned pesticide residues in soil samples is a matter of concern for future food chain accumulation and human health also. So, regular investigation of pesticide residues is required. We need to find out alternative solutions and stronger regulations. Survey results indicated that farmers with low education levels used highly toxic pesticides. Farmers reported that they did not always use pesticides in an appropriate manner. These improper practices may result in the contamination of the environment by pesticides. This article can help farmers in spray of pesticides as few as possible because, many pesticides are toxic and more stable so that avoidance of these pesticides can reduce the contamination of Pesticides in soil and also can help to prevent the financial loss of farmer and exporter too.

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